Synthetic lubricant basestocks from epoxidized soybean oil and Guerbet alcohols

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Abstract

Vegetable oils are biodegradable and therefore good candidates for environmentally friendly base stocks. They have excellent lubricity, but poor oxidation and low temperature stabilities. For this study, synthetic lubricant basestocks with oxidative stabilities and pour points comparable with commercial synthetic lubricant basestocks have been prepared by reacting epoxidized soybean oil with Guerbet alcohols. Four different Guerbet alcohols, C12-, C14-, C16-, and C18-Guerbet alcohols were used. Reaction of epoxidized soybean oil with a Guerbet alcohol in the presence of a catalytic amount of sulfuric acid provided open-ringed products. ^{1}H NMR has shown that transesterification follows after ring-opening reaction under the given reaction conditions. Two types of ring-opened products, 0%- and 100%-transesterified products, could be obtained under controlled reaction conditions. Pour points of the ring-opened products ranged from −18 to −36 °C without pour point depressant (PPD) and from −21 to −42 °C with 1% of PPD. Acetylation of hydroxy groups in the ring-opened products further lowered pour points that ranged from −27 to −42 °C without PPD and from −30 to −48 °C with 1% of PPD. Oxidative stability was examined using a modified Penn State microoxidation test and compared with those of synthetic lubricant basestocks and mineral oil. Oxidative evaporations of two selected products in the microoxidation test were similar to mineral oil and less than synthetic lubricant-based oils, polyalphaolefin (PAO$_4$) and diisododecyl adipate. Deposits of these products were similar to synthetic lubricant-based oils and less than mineral oil.
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1. Introduction

Vegetable oils have been attractive renewable resources for environmentally friendly lubricants because of their biodegradability, outstanding lubricating properties, high viscosity indices, low volatility, and high flash points (Legarand and Dürr, 1998). In spite of their many advantages, two major problems of vegetable oils, inadequate oxidative stability and poor low-temperature properties, are obstacles to their utilization as lubricant basestocks (Asadauskas et al., 1996; Erhan and Asadauskas, 2000). Chemical modification of vegetable oils is an attractive way to solve these problems. Transforming alkene groups in a vegetable oil to other stable functional groups could improve the oxidative stability, whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve low-temperature performance. Our previous study has

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[1] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of other that may also be suitable.

already shown that ring-opening reaction of the epoxidized soybean oil with an alcohol followed by esterification of resulting hydroxy groups improves their oxidative stabilities and pour points (Hwang and Erhan, 2001).

Guerbet alcohols were first synthesized by Marcel Guerbet in 1899 by a modified aldol condensation of alcohols followed by subsequent hydrogenation (Fanelli, 1988; Knothe and Carlson, 1998). The resulting products are branched saturated alcohols of essentially twice the molecular weight of the starting alcohols. Because of their excellent lubricating properties, low pour points, and low volatility, Guerbet alcohols and their derivatives including Guerbet esters are used as components in various commercial products such as hydraulic fluids (Mueller et al., 1996).

Based on previous research on the development of soybean oil-based lubricants, our objective was to prepare synthetic lubricant basestocks from epoxidized soybean oil and Guerbet alcohols. The pour point, viscosity, viscosity index, and oxidative stability in microoxidation test were evaluated to investigate the effect of structural variation in the oil molecules.

2. Materials and methods

2.1. Materials

The epoxidized soybean oil (ESO, 100% epoxidized) was purchased from Elf Atochem Inc. (Philadelphia, PA) and used as received. Guerbet alcohols were obtained from Jarchem Industries Inc. (Newark, NJ) and used without further purification. The trade names, Jarcol, will be used for Guerbet alcohols in this paper. Jarcol I-12 is 2-butyl octanol, Jarcol I-14T is a mixture of 2-butyl decanol, 2-hexyl octanol, and their analogs (C_{12} 10–20%, C_{14} 45–55%, C_{16} 25–35%), Jarcol I-16 is 2-hexyl decanol, and Jarcol I-18T is a mixture of 2-octyl decanol, 2-hexyl dodecanol, and their analogs (C_{16} 15–20%, C_{18} 46–54%, C_{20} 27–33%). A polyalphaolefin, PAO4 (notation 4 indicates approximate kinematic viscosity in cSt at 100 °C and differentiates it from PAO2, PAO6, PAO10, etc.) was obtained from Amoco (Lisle, IL). Acetic anhydride, pyridine, and diisododecyl adipate (99% purity) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. All solvents were purchased from Fisher Scientific Co. (St. Louis, MO) and used as received.

2.2. Analysis

^{1}H NMR spectra were taken with a Bruker (Rheinstetten, Germany) ARX 400 spectrometer. Fourier Transform-Infrared (FT-IR) spectra were obtained with a Perkin-Elmer (Bucks, England) Spectrum RX FT-IR System as film on NaCl plates.

2.3. Ring-opening reaction

A mixture of epoxidized soybean oil (100 g, 0.47 mole of epoxy groups) and a Guerbet alcohol (0.47 mole for a 0%-transesterified products or 0.61 mol for a 100%-transesterified product) was heated at 90 °C with stirring. Sulfuric acid (40 drops) was added dropwise and the mixture was stirred at 110 °C for 0%-transesterified products or at 120 °C for 100%-transesterified products for 20 h. The reaction mixture was cooled by adding ice and saturated aqueous sodium bicarbonate (100 ml) was added. The mixture was extracted with ethyl acetate (200 ml), dried over anhydrous magnesium sulfate, filtered, and evaporated using a rotary evaporator. Any volatile materials including the remaining solvent were evaporated under vacuum (41.37–68.95 Pa) at 80 °C overnight to give the ring-opened product.

2.4. Acetylation of the ring-opened product

To a mixture of the ring-opened product (50 g) and acetic anhydride (16 ml, 0.15 mol), pyridine (14 ml, 0.15 mol) was added dropwise and the mixture was stirred at 80 °C for 2 h under a nitrogen atmosphere. The reaction mixture was cooled with ice water (200 ml) and then extracted with ethyl acetate (200 ml). The organic layer was washed successively with 5% NaOH (100 ml), 5% HCl (100 ml), and 5% aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and evaporated using a rotary evaporator. The remaining solvent and other volatile components were removed under vacuum (41.37–68.95 Pa) at 80 °C overnight to give the product.

2.5. Pour point measurement

The pour points were determined by ASTM D 97 (ASTM, 2000a) with an accuracy of ±3 °C with the Cloud and Pour Point Test apparatus [Petrolab Corporation, Latham, New York]. Test jars, thermometers, corks, and rubber rings fully met ASTM D 97 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in 3 °C increments at the top of the sample until it stopped pouring. The temperature of

cooling media was kept constant at -18, -33, -51, and $-69\,^{\circ}\text{C}$ as the sample temperatures reached -6, -24, -42, and $-48\,^{\circ}\text{C}$, respectively.

2.6. Viscosity measurement

Viscosity measurements were made at 40.0 and 100.0 °C using calibrated Cannon-Fenske viscometer tubes in a Cannon CT-1000 Constant Temperature viscosity bath (Cannon Instrument Co., State College, PA). Viscosity and viscosity index were calculated using ASTM D 445 and ASTM D 2270 methods, respectively (ASTM, 2000b,c). All viscosity measurements were run in duplicate and the average value was reported.

2.7. Microoxidation test

Experiments were carried out using the Penn State Microoxidation Kit (Perez et al., 1987; Lee et al., 1993). A small amount of oil ($20\,\mu$l) was placed on an activated high carbon steel catalyst to make a thin film. The catalyst with the test oil was placed on a hot plate, which maintained the temperature at $175 \pm 1\,^{\circ}\text{C}$. An air flow of $20\,\text{cm}^3$/min was maintained over the sample. After a specified time, the catalyst with oxidized oil was removed from the oxidation chamber and weighed to determine sample loss by oxidative volatility. After cooling to room temperature, the catalyst was soaked in tetrahydrofuran (THF, 20 ml) for 30 min to dissolve out the soluble portion of the oxidized oil. The catalyst containing the insoluble deposit was placed in a desiccator to dry and then weighed to determine the insoluble deposit.

3. Results and discussion

Epoxidized soybean oil (ESO) was reacted with a Guerbet alcohol in the presence of a catalytic amount of concentrated sulfuric acid (0.5 ml/100 g of ESO). Completion of ring-opening reaction was confirmed by checking the disappearance of epoxy signals at 1158, 845 and 822 cm^{-1} in the IR spectrum. Transesterification followed ring-opening under the reaction conditions used in this study as shown in Fig. 1. Many other different types of minor products such as oligomers obtained by intra- and intermolecular epoxy–epoxy reactions may exist in the product and reported in another paper (Hwang and Erhan, 2001). This paper will mainly discuss the preparation, pour point, oxidative stability, and viscosity of the products.

^{1}H NMR has verified the reaction sequence of ring-opening followed by transesterification at 130 °C when
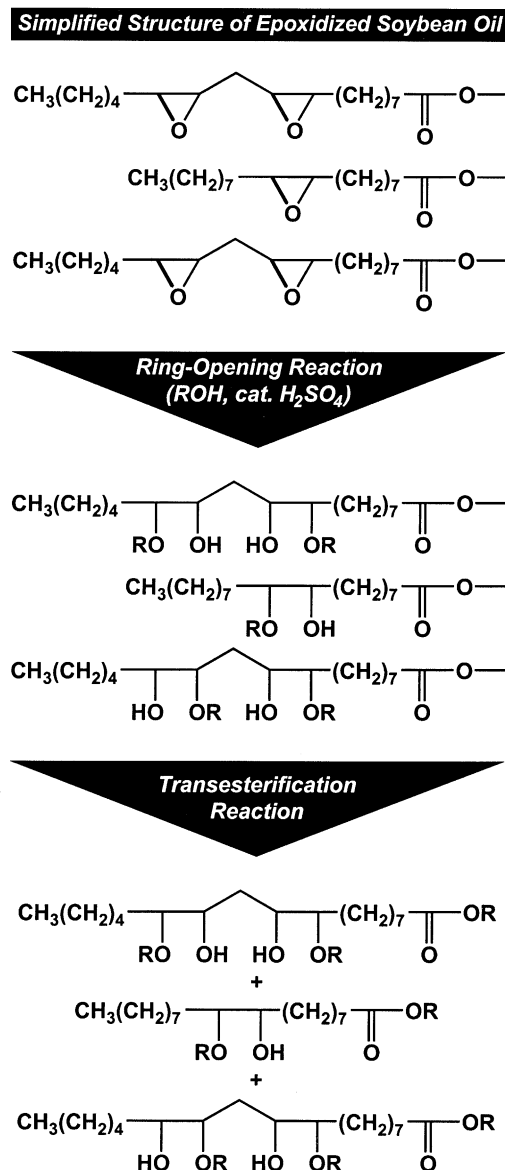

Fig. 1. Reaction scheme of ring-opening reaction followed by transesterification of epoxidized soybean oil with a Guerbet alcohol.

1.6 equivalents of Jarcol I-18T to the epoxy groups in ESO was used (1.6 equivalents of Jarcol means 1.6 times larger molar amounts compared with epoxy groups in ESO). The change in the ^{1}H NMR spectrum with reaction time are shown in Fig. 2. Fig. 2A shows the NMR spectrum of the mixture of the starting materials, ESO and Jarcol I-18T. The ring-opening reaction was monitored by the disappearence of epoxy ring hydrogen (H$_A$). After 2.5 h reaction time period, 97% of ring-opening reation was completed whereas no transesterification occurred (Fig. 2B). The transesterification was moni-
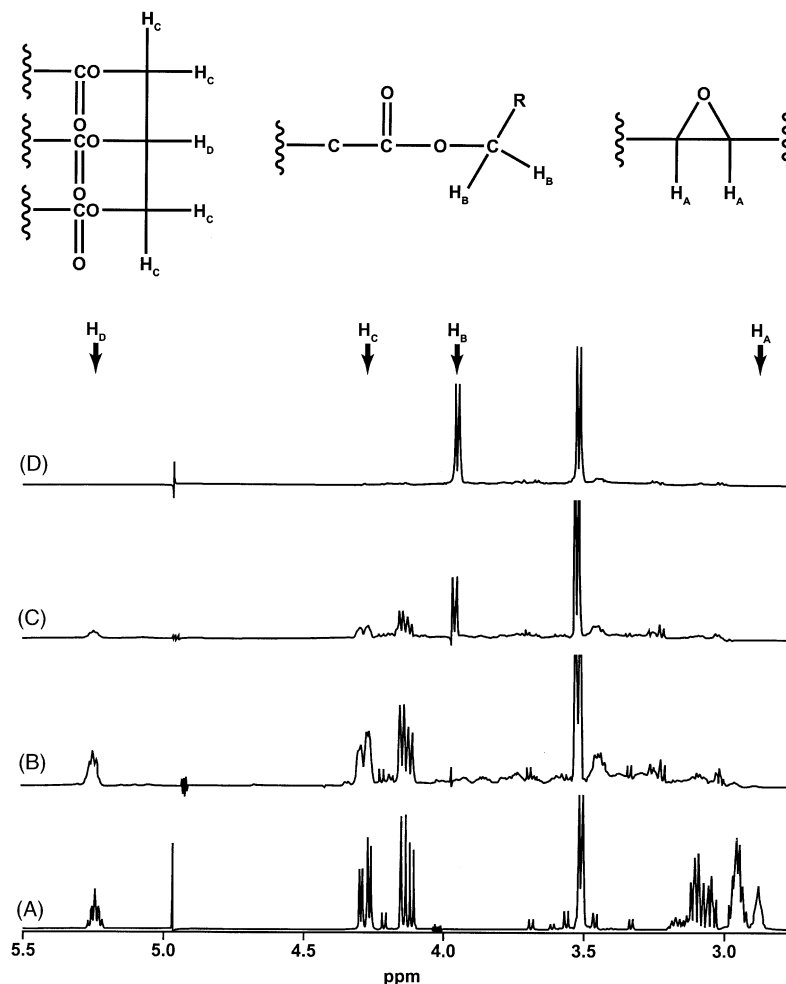
Fig. 2. Spectral changes in ^{1}H NMR for the reaction of epoxidized soybean oil with Jarcol I-18T (1.6 equivalents) at 130 °C with reaction times of (A) 0 h, (B) 2.5 h, (C) 4 h, and (D) 7 h.

tored by the appearance of signals for the alkyl hydrogen alpha to the ester oxygen atom derived from the alcohol portion of the newly formed esters alpha proton (H_B) and also by the disappearence of hydrogen signals of triacylglycerol backbone (H_C and H_D). After the reaction time of 4 h, the area of the hydrogen signals inherent to the triacylglycerol backbone (H_C and H_D) decreased and a signal of alpha hydrogen (H_B) of the transesterifed product appeared (Fig. 2C). After a prolonged reaction time (7 h), all the triacylglycerol backbone hydrogen signals disappeared (Fig. 2D). Fig. 3 depicts the reaction rates of ring-opening and transesterification of ESO with Jarcol I-18T.

In this study, interest was directed that to the two representative products, 100%-ring opened/0%-transesterified product and 100%-ring opened/100%-transesterified product due to their convenient
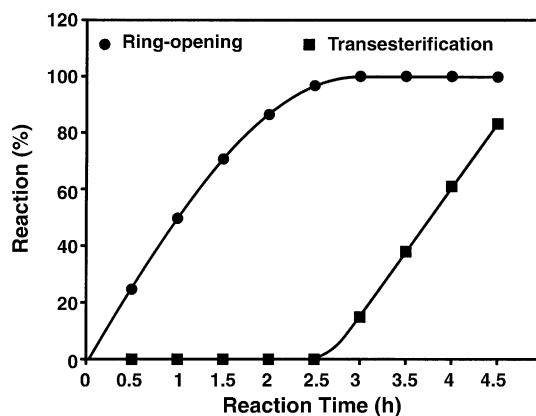

Fig. 3. Ring-opening vs. transesterification in the reaction of epoxidized soybean oil with Jarcol I-18T (1.6 equivalents) at 130 °C.

Table 1
Pour points, viscosities, and viscosity indices of ring-opened products

Product	Alcohol	*Trans*-esterification (%)	Pour points (°C) with			Viscosity (cSt)		VI
			0% PPD	0.5% PPD	1% PPD	40 °C	100 °C	
1	Jarcol I-12	0	−18	−18	−21	204.3	20.0	113
2	Jarcol I-14T	0	−18	−18	−21	221.7	20.0	104
3	Jarcol I-16	0	−18	−18	−21	232.4	20.9	106
4	Jarcol I-18T	0	−18	−18	−21	195.6	16.4	86
5	Jarcol I-12	100	−27	−39	−42	64.6	8.3	96
6	Jarcol I-14T	100	−36	−36	−36	59.6	8.3	109
7	Jarcol I-16	100	−36	−36	−36	60.5	8.6	115
8	Jarcol I-18T	100	−30	−33	−36	74.5	10.3	122
PAO4			−66	−66	−69	17.7	4.0	125
Diisododecyl adipate			−63	−66	−69	14.5	3.6	135
Epoxidized soybean oil			0	0	0	–	–	–

preparations (hereinafter the former is referred to as 0%-transesterifed product and the later 100%-transesterified product). When 1.0 equivalent of Guerbet alcohol to the epoxy groups in ESO was used in the reaction at 110 °C for 20 h, the 0%-transesterified product was obtained. Even after a longer reaction time (30 h), no trace of transesterified product was found. On the other hand, reaction of ESO with 1.3 equivalents of Guerbet alcohol at 120 °C for 20 h provided the 100%-transesterified product. Eight different ring-opened products were prepared with four different Guerbet alcohols including Jarcol I-12, Jarcol I-14T, Jarcol I-16, and Jarcol I-18T.

Pour points, viscosities, and viscosity indices of the products (**1–8**) were determined using ASTM D 97, ASTM D 445, and ASTM D 2270 standard methods, respectively. The pour points of 0%-transesterified products (**1–4**) were measured at −18 °C, −18 °C, and −21 °C with 0, 0.5, and 1% of PPD, respectively are listed in Table 1. Viscosities of the products ranged from

195.6 to 232.4 cSt at 40 °C, and from 16.4 to 20.9 cSt 100 °C.

Pour points of the 100%-transesterified products (**5–8**) are lower (−27 to −36 °C) than those of the 0%-transesterified products. Adding 1% of PPD showed no remarkable effect with the exception of product **5**, which decreased pour point by −42 °C with 1% of PPD. The 100%-transesterified products (**5–8**) have lower viscosities (59.6–74.5 cSt at 40 °C and 8.3–10.3 cSt at 100 °C) than the corresponding 0%-transesterified products (**1–4**). Viscosity indices were measured at 86–113 for 0%-transesterified products and 96–122 for 100%-transesterified products.

We observed previously that esterification of the resulting hydroxy groups in a ring-opened product lowers the pour point (Hwang and Erhan, 2001). The hydroxy groups in the ring-opened products **1–8** were esterified with acetic anhydride and pyridine to give acetylated products **9–16**. Pour point depression by acetylation is shown in Table 2 and the lowest pour point

Table 2
Pour points, viscosities, and viscosity indices of acetylated products

Product	Guerbet alcohol	*Trans*-esterification (%)	Pour points (°C) with			Viscosity (cSt)		VI
			0% PPD	0.5% PPD	1% PPD	40 °C	100 °C	
9	Jarcol I-12	0	−27	−27	−30	102.8	14.6	147
10	Jarcol I-14T	0	−30	−30	−30	103.4	13.9	136
11	Jarcol I-16	0	−27	−30	−30	103.0	14.1	139
12	Jarcol I-18T	0	−33	−33	−36	74.3	11.7	152
13	Jarcol I-12	100	−27	−42	−45	35.6	6.5	137
14	Jarcol I-14T	100	−33	−45	−48	36.6	6.7	141
15	Jarcol I-16	100	−42	−45	−48	38.4	7.1	149
16	Jarcol I-18T	100	−42	−45	−48	41.5	7.5	149
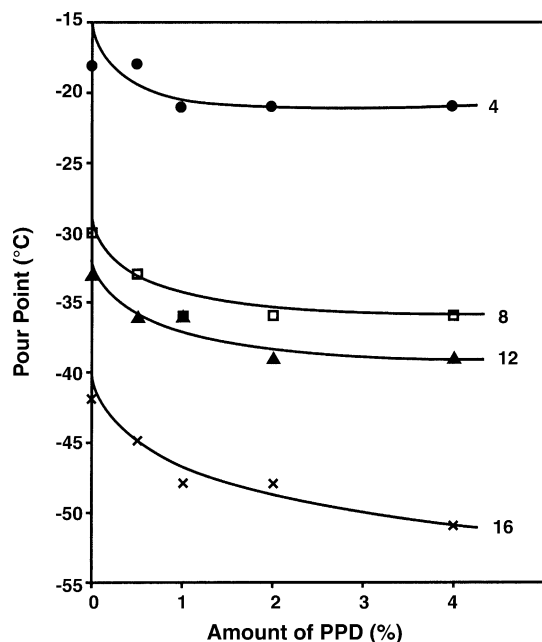
Fig. 4. Effect of the amount of PPD in pour point depression of products **4**, **8**, **12**, and **16**.

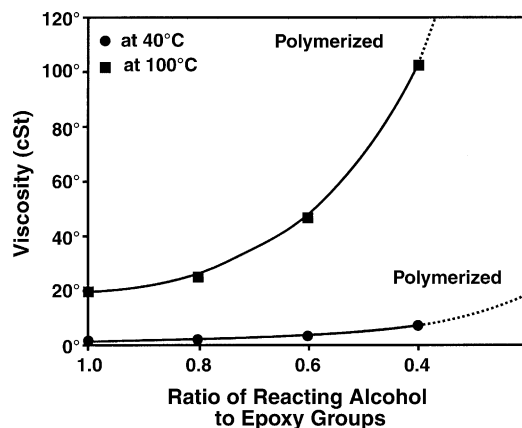Fig. 5. Relationship between viscosity and the amount of reacting Guerbet alcohol.
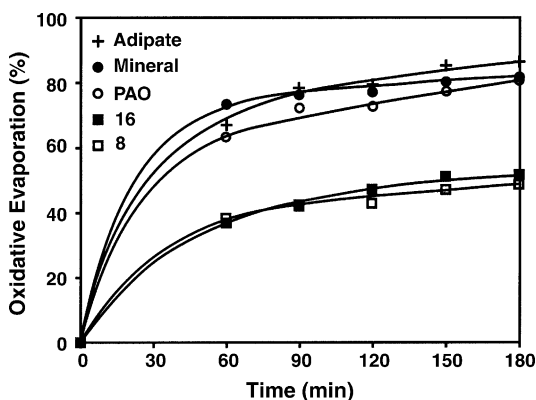
Fig. 6. Oxidative evaporation in microoxidation test.

Fig. 7. Insoluble deposits in microoxidation test.

was observed at $-48\,^{\circ}$C for **14**, **15**, and **16** in the presence of PPD (1%). The acetylated products have lower viscosities and higher viscosity indices than products before acetylation.

To investigate the pour point depression with different amounts of PPD, pour points of four different products **4**, **8**, **12**, and **16** were measured with 0, 0.5, 1, 2, and 4% of PPD (Fig. 4). The pour point decreased rapidly until 1% of PPD, beyond which there was no dramatic effect of PPD concentration on pour point.

To study the effect of the amount of alcohol used in the reaction on a product's viscosity, different amounts (1.0, 0.8, 0.6, 0.4, and 0.2 equivalents to the epoxy groups in ESO) of Jarcol I-18T were reacted to ESO. The reaction was conducted at $120\,^{\circ}$C and quenched after the completion of ring-opening and before the transesterification reaction to give 0%-transesterified products. As shown in Fig. 5, when the amount of reacting alcohol decreased, viscosities of the products increased. When 0.2 equivalents of alcohol were used, a gel-like polymer was obtained. When a smaller amount of alcohol is used, more inter- and intramolecular reactions between epoxy groups occur to produce high molecular weight products that result in higher viscosity.

A modified Penn State microoxidation test was used to determine oxidative stability of the products **8** and **16**. The test was performed at $175\,^{\circ}$C on a high carbon steel catalyst and samples were analyzed after 60,

90, 120, 150, and 180 min of oxidation. Oxidative evaporation of the product is shown in Fig. 6. Thus, the evaporation of a sample is caused not only by simple evaporation by heat, but also by other chemical reactions such as thermal decomposition and *cis*-elimination
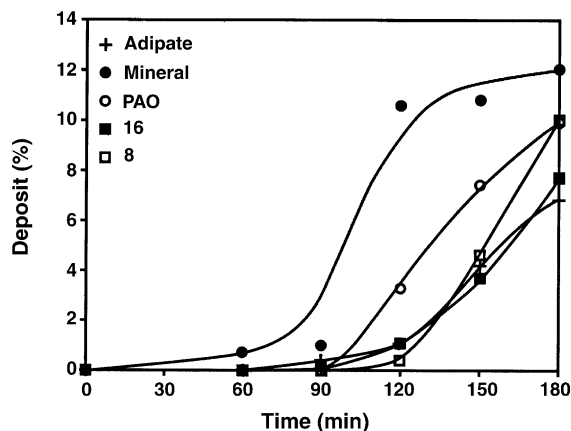
of ester groups to produce volatile materials (Palekar et al., 1995). Oxidative evaporation of products **8** and **16** are similar to mineral oil and lower than commercial synthetic lubricant basestocks, polyalphaolefin (PAO4) and adipate (diisododecyl adipate). Deposits obtained after 180-min microoxidation of the two products (**8** and **16**) are much less than mineral oil and similar to PAO and adipate as shown in Fig. 7.

4. Conclusions

Synthetic lubricant basestocks were prepared by the reaction of epoxidized soybean oil with Guerbet alcohols. The lowest pour points were observed at $-42\,^{\circ}C$ for the acetylated 100%-transesterified products with Jarcol I-16 and Jarcol I-18T. Further improvement in the pour points of these compounds can be achieved by using suitable pour point depressant (PPD) additives. The PPD concentration was optimized by determining the pour point and low temperature stability of several blends. The purpose of PPD is to hinder crystallization of triacylgycerol molecules at low temperature by further disrupting the stacking mechanism. An optimum PPD concentration of 1% was able to lower the pour point to $-48\,^{\circ}C$. Further addition of PPD made no significant improvement in the pour point.

The modified Penn State microoxidation test showed that the products have oxidative stabilities comparable with those of synthetic lubricant basestocks, PAO4 and diisododecyl adipate.

Acknowledgement

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